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VISUAL APPEARANCE OF POLYMERIC CONTAMINATION

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| 16. Abstract This paper presents a series of photomicrographs which shows the condensate that a selected group of polymers might have if they were present as spacecraft contaminants. Nine classes of polymeric materials were subjected to temperature and vacuum conditions, and, using microscopic techniques, the condensed effluents were observed. Outgassing data are presented for some materials in the form of weight loss. Photographic material is presented for seven classes; however, for the remaining two classes, the techniques appeared inapplicable. The concept that the appearance of condensate might be unique for each class of polymer is of limited value. The condensate pattern varied as a function of the temperature of the base material for all except one of the seven classes that were photographed. The similarity in the patterns of several classes of polymers makes identification of a particular species problematic. | | | |
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CONTENTS

| | Page |
|---|------|
| INTRODUCTION | 1 |
| APPARATUS AND EXPERIMENTAL PROCEDURES | 2 |
| RESULTS | 3 |
| Polyimide | 3 |
| Methyl Methacrylate | 3 |
| Polyethylene Terephthalate | 5 |
| Expanded Polyethylene | 7 |
| Polystyrene | 7 |
| Polyvinyl Chloride | 8 |
| Polyurethane | 10 |
| Epoxy and RTV | 10 |
| DISCUSSION | 11 |
| CONCLUSIONS | 12 |

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INTRODUCTION

It has been shown* that DC 704 diffusion pump oil might backstream by first forming droplets and then reevaporating and recondenasing. This mechanism was sufficiently different from the expected film formation and creep that the modes of contamination of other materials were questioned. The techniques found in the earlier work were simplified and applied to a range of polymeric materials, a number of which are commonly used in spacecraft applications.

This study attempts to examine the outgassing effluent of different classes of polymeric materials. No attempt is made to study the effects of varying the different possible parameters within the class. It was considered impractical to attempt to characterize the variables of cure such as time, temperature, and percent of accelerator for the various plastic materials, and no effort is made to rank the materials "good or bad." It was hoped that each class of polymer would exhibit some unique condensate which would permit easy and quick identification. This goal was partially achieved, and where the condensate is in some form other than droplets, as for the urethanes, identification is greatly facilitated. Where the condensate was in droplet form, difficulty was encountered in distinguishing between materials.

Time, temperature, and pressure are the operating parameters. In addition, for some experiments, weight loss is also given; however, no good correlation between weight loss and a visible contaminant could be found. The nature of the condensable effluent is not determined for any case. In the work with polyvinyl chloride (PVC), efforts were made to determine the chemical class of the condensate. Infrared analysis and gas chromatography were two analytical methods attempted. No chemical identification was made of the minute quantities with which this work is concerned.

*Shapiro, H., and Hanyok, J., "Monomolecular Contamination of Optical Surfaces," *Vacuum*, Vol. 18, No. 11, pp. 587-592, 1968.

It is not here suggested that the data presented reflect what may be found as effluent from a spacecraft under test or in orbit. Many of the experimental conditions would seldom be met, as for example, 300°C in an unsuccessful attempt to find an effluent from the epoxy material. To those interested in the possibility of contaminating sensitive surfaces, the study presents a very sensitive method for finding such contamination and, in at least some instances, a method of identification.

APPARATUS AND EXPERIMENTAL PROCEDURES

Most of the equipment used for this study was of the simplest kind. A stainless steel chamber, 12 in. long by 8 in. in diameter, with the necessary plumbing to attach a mechanical pump, constituted the basic vacuum chamber. Additional piping was used to attach a small diffusion pump, which was used where pressures lower than those produced by a mechanical pump were required. An ordinary glass microscope slide, clamped about 3 in. above the oven, served as the collector. The oven was a 1-1/2-in. stainless steel cube with a 1-1/4-in. cavity drilled in the center. Five resistors, connected in series, were mounted on the sides and bottom to supply the required heat. Thermocouples, which supplied the temperature data, were held in place on the oven by screws to provide good contact. Weight loss data, to the fifth decimal place, were taken with a Cahn electrobalance.

The general procedure used in the experimental work was to subdivide the experimental polymer to some convenient size. In the case of PVC, this consisted of cutting sheet stock with scissors; in the case of epoxy, it meant breaking the material into small pieces with a hammer and chisel. The weights of the pieces ranged from 5 g for the epoxy material to 0.3 g for Mylar film. When a suitably subdivided sample was selected, that sample was used to obtain all the data presented for its polymeric class. The pieces were transferred to the oven, the collector was placed above the oven, and the chamber was closed. The chamber was then evacuated to the desired degree of vacuum for the desired length of time. At the end of the time period, the procedure was reversed. The weight loss was recorded, and the collector was examined under a microscope.

The collector was carefully cleaned to show no water break and was examined under a microscope for visible nucleation sites, such as dust and lint. The collector was then placed in position and brought under vacuum as soon as possible. At frequent intervals throughout the course of the experiment, blank slides were exposed to the empty chamber to verify chamber cleanliness.

Estimates of the amount of effluent, as seen on the collector under 1400 \times magnification, were based upon the shift in frequency of a quartz-crystal microbalance built small enough to fit conveniently into the body of the vacuum chamber. The crystals, together with most of the required electronics, were enclosed in a 2-in. \times 2-in. \times 3-in. package which could be hung in any part of the chamber. Considerable experimentation and manipulation were required to obtain some measure of the quantities involved.

RESULTS

The data from this investigation and photomicrographs of seven classes of polymers are given below.

Polyimide

A polyimide sample cut from 0.001-in. film stock was heated to 100°C for 40 hours at 10 μ pressure (Figure 1). The sample was then subjected to 200°C for 20 hours at the same pressure (Figure 2). No weight loss data were obtained.

Subsequently, the sample was heated to 100°C for 20 hours at a reduced pressure of 10 $^{-6}$ torr without evidence of effluent accumulation. The conditions described in Figure 1 were duplicated on the same sample without further effluent accumulation.

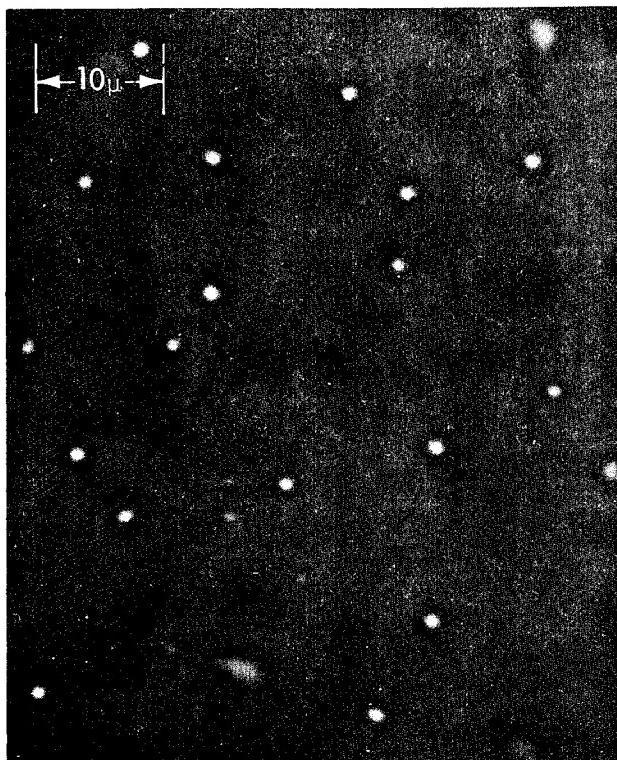


Figure 1—Effluent accumulation from polyimide after sample was heated to 100°C for 40 hours at 10 μ pressure.

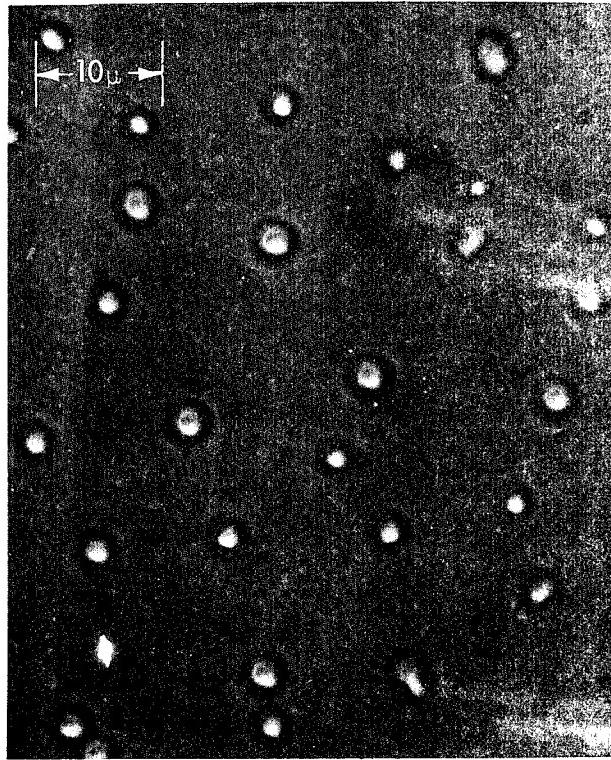


Figure 2—Effluent accumulation from polyimide after sample was heated to 200°C for 20 hours at 10 μ pressure.

Methyl Methacrylate

A 1.0-g sample of methyl methacrylate consisting of small chips broken from 1/4-in. sheet stock was subjected to five measurements. The test conditions and results are listed in Table 1. Photomicrographs of the third, fourth, and fifth tests are shown in Figures 3, 4, and 5, respectively.

Table 1—Methyl Methacrylate.

| Test | Temperature (°C) | Pressure (μ) | Time (hours) | Weight loss (%) | Contaminants |
|------|---------------------|-----------------------|-----------------|-----------------------|--------------|
| 1 | 50 | 10 | 1 | 0.08 | No |
| 2 | 100 | 10 | 16 | 0.30 | No |
| 3 | 170 | 10 | 16 | 0.37 | Yes |
| 4 | 170 | 10 | 1 | 0.00 | Yes |
| 5 | 200 | 10 | 1 | 0.05 | Yes |

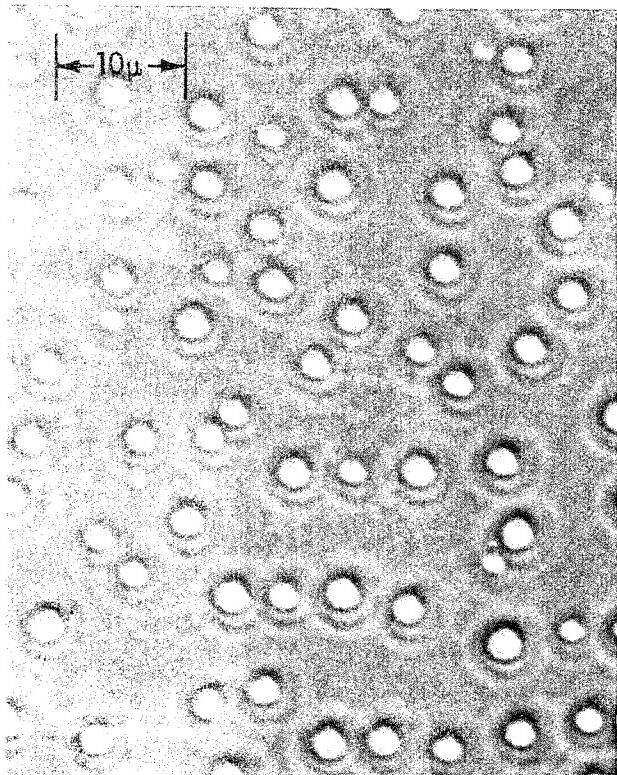


Figure 3—Effluent accumulation from sample after methyl methacrylate was heated to 170° C for 16 hours at 10μ pressure.

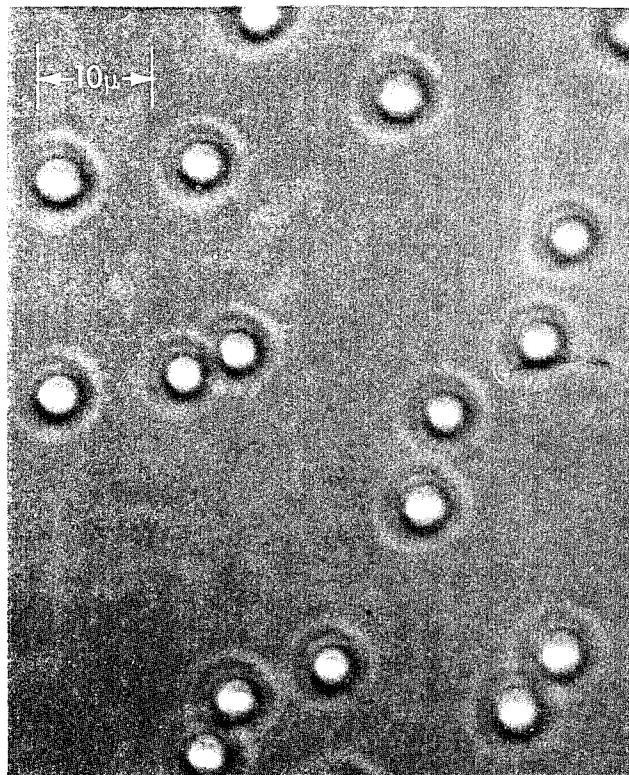


Figure 4—Effluent accumulation from sample after methyl methacrylate was heated to 170° C for 1 hour at 10μ pressure.

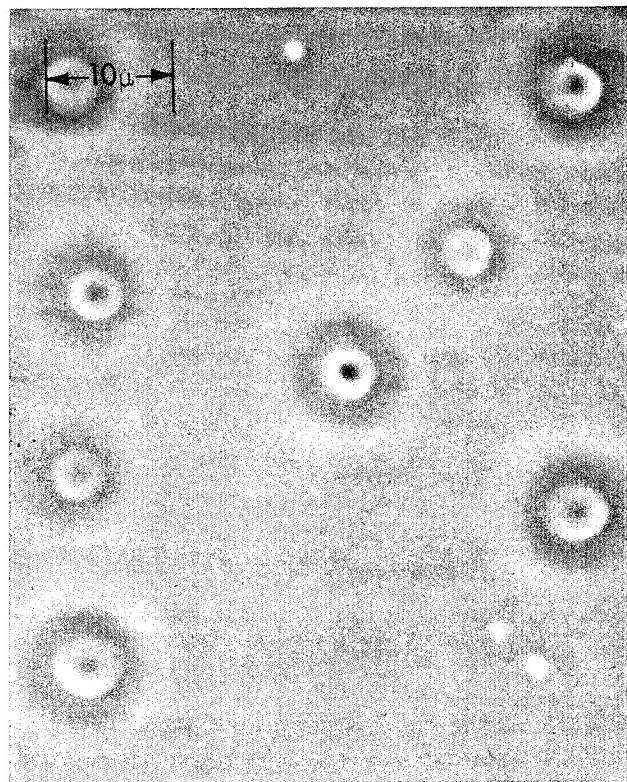
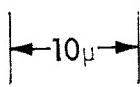


Figure 5—Effluent accumulation from sample after methyl methacrylate was heated to 200° C for 1 hour at 10 μ pressure.

Figure 6—Polyethylene terephthalate effluent after sample was heated to 150° C for 65 hours at 15 μ pressure.

Polyethylene Terephthalate

A sample of polyethylene terephthalate cut from 0.0015-in. Mylar film and weighing 0.4 g was observed under three test conditions. The results are tabulated in Table 2 and shown in Figures 6, 7, and 8.

Table 2—Polyethylene Terephthalate.

| Test | Temperature (°C) | Pressure (μ) | Time (hours) | Weight loss (%) |
|------|---------------------|-----------------------|-----------------|--------------------|
| 1 | 150 | 15 | 65 | 0.15 |
| 2 | 150 | 10 | 3 | 0.13 |
| 3 | 220 | 10 | 1 | No data |

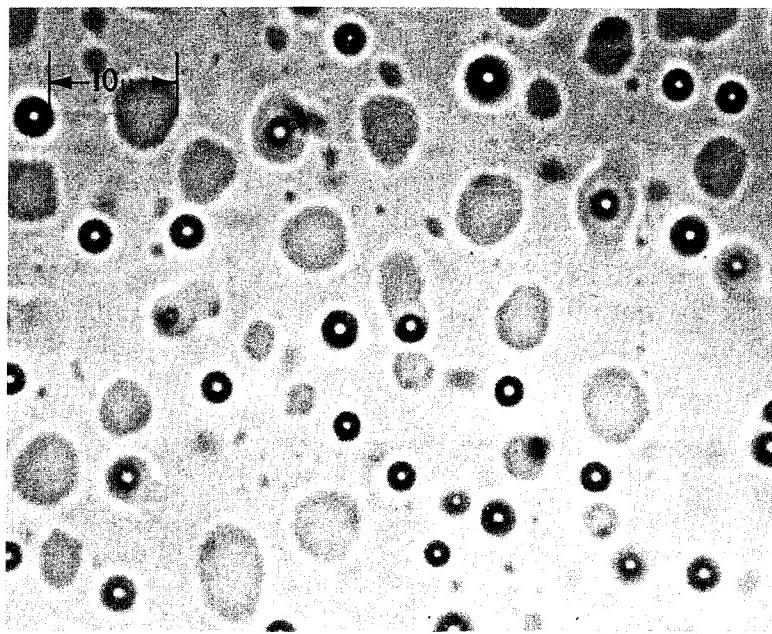


Figure 7—Polyethylene terephthalate effluent after sample was heated to 150° C for 3 hours at 10 μ pressure.

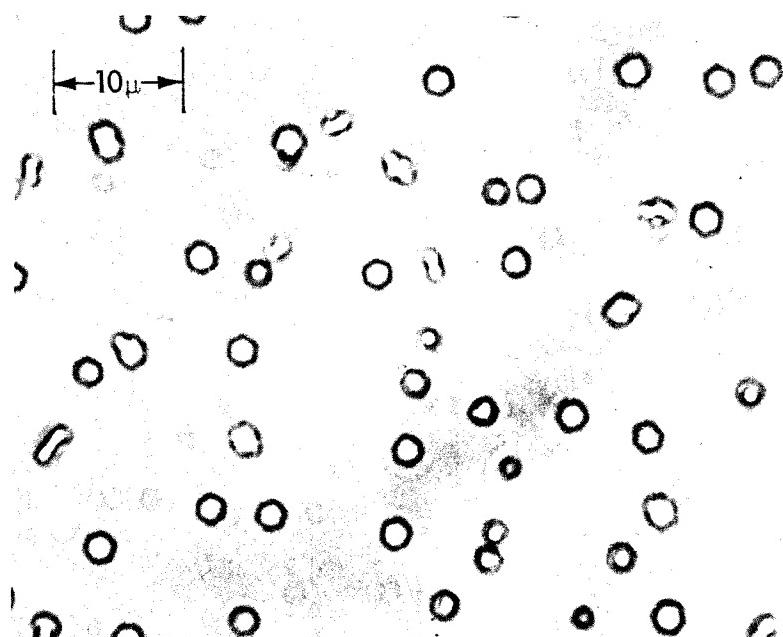


Figure 8—Polyethylene terephthalate effluent after sample was heated to 220° C for 1 hour at 10 μ pressure.

Expanded Polyethylene

Four experiments were performed on a 0.7-g sample of expanded polyethylene taken from a 1/2-in. cube. Temperature was varied from 100° to 220°C; pressure was varied from 10μ to 10^{-6} torr. During each of three experiments, a weight loss of 0.25% was observed without visible contamination. The expanded form melted at 170°C, and the droplets shown in Figure 9 formed. The weight loss for that run was 0.34%.

Each of the four variations was continued for 3 hours, after which the samples were allowed to cool to room temperature. The hard plastic material remaining showed no further reactions.

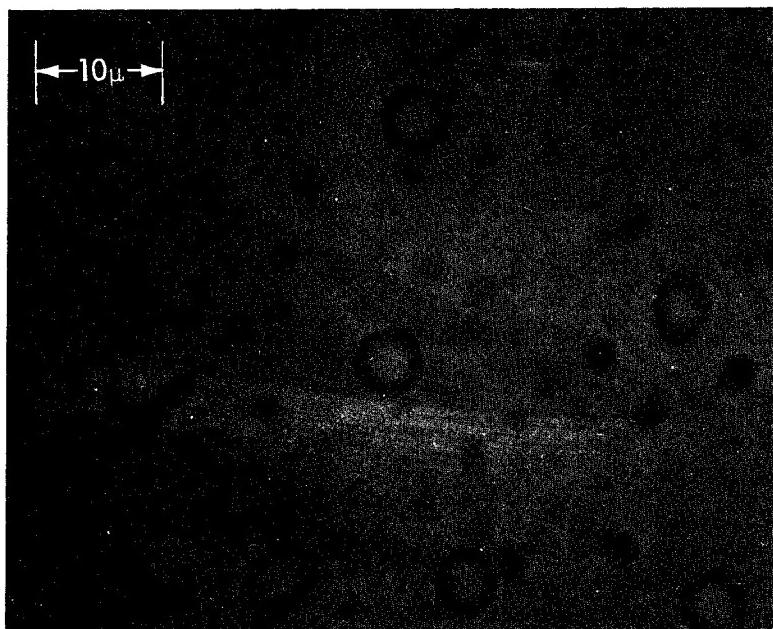


Figure 9—Photomicrograph of droplets that formed on collector when expanded polyethylene melted at 170°C.

Polystyrene

A 2.0-g sample of small pieces of polystyrene shaved from rod stock was subjected to three runs. The results of the three runs are listed in Table 3; Figures 10 and 11 show the results of runs 1 and 2, respectively.

Table 3—Polystyrene.

| Test | Temperature (°C) | Pressure (μ) | Time (hours) | Weight loss (%) |
|------|---------------------|-----------------------|-----------------|--------------------|
| 1 | 75 | 10 | 1 | 0.01 |
| 2 | 100 | 10 | 1 | 0.02 |
| 3 | 55 | 10 | 16 | 0.01 |

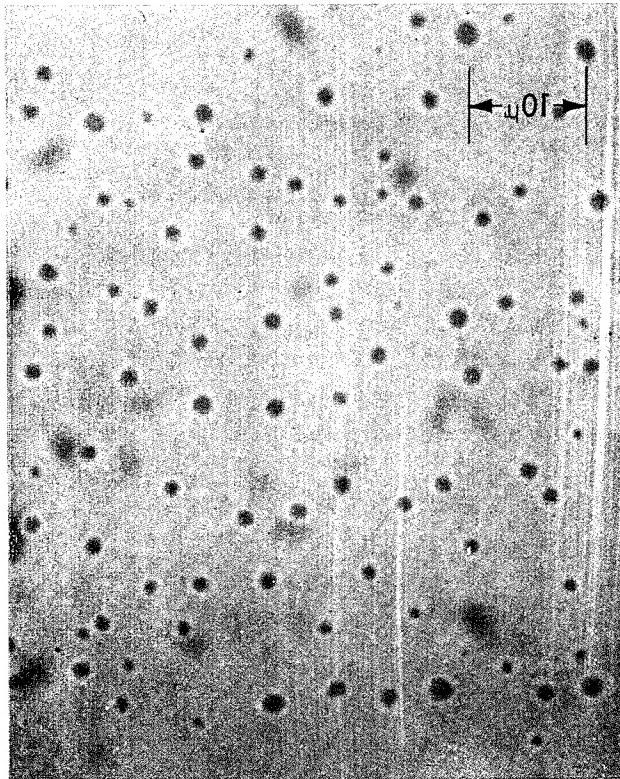


Figure 10—Polystyrene effluent after sample was heated to 75° C for 1 hour at 10 μ pressure.

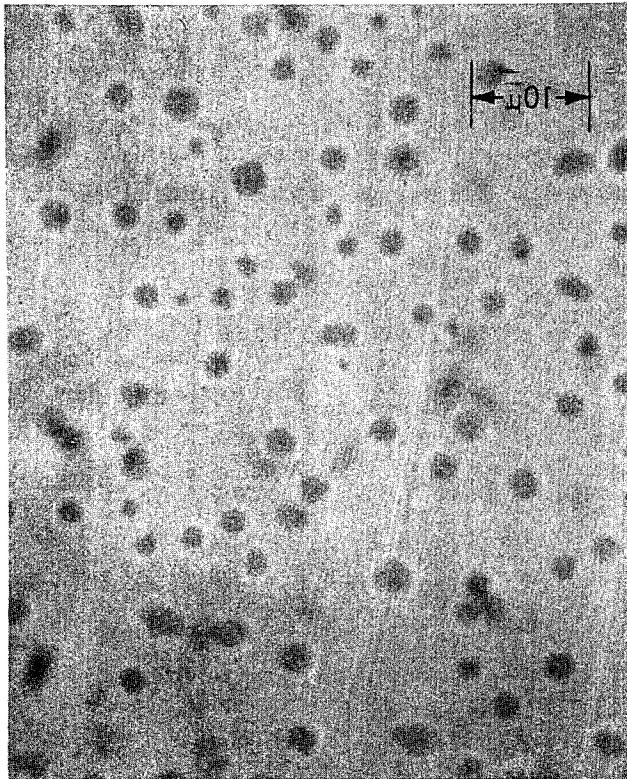


Figure 11—Polystyrene effluent after sample was heated to 100° C for 1 hour at 10 μ pressure.

Polyvinyl Chloride

A polyvinyl chloride sample consisting of small pieces cut from sheet stock was subjected to eight tests, the results of which are listed in Table 4. No weight loss data were taken on any of the tests.

Table 4—Polyvinyl Chloride.

| Test | Temperature (°C) | Pressure | Time | Contamination |
|------|---------------------|-----------------------|--------|---------------|
| 1 | 23 | 50 μ | 5 min | No |
| 2 | 23 | 20 μ | 1 hr | No |
| 3 | 23 | 10 ⁻⁵ torr | 2 hr | No |
| 4 | 50 | 20 μ | 30 min | No |
| 5 | 50 | 20 μ | 16 hr | No |
| 6 | 60 | 10 μ | 16 hr | No |
| 7 | 70 | 15 μ | 1 hr | Droplets |
| 8 | 70 | 15 μ | 3 hr | Droplets |

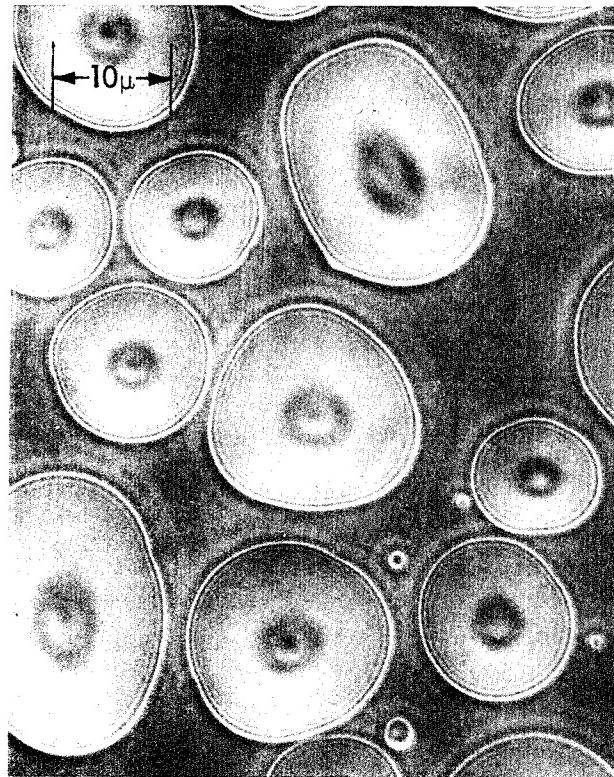


Figure 12—Photomicrograph of droplets that formed on collector when polyvinyl chloride sample was heated to 70° C for 1 hour at 15 μ pressure.

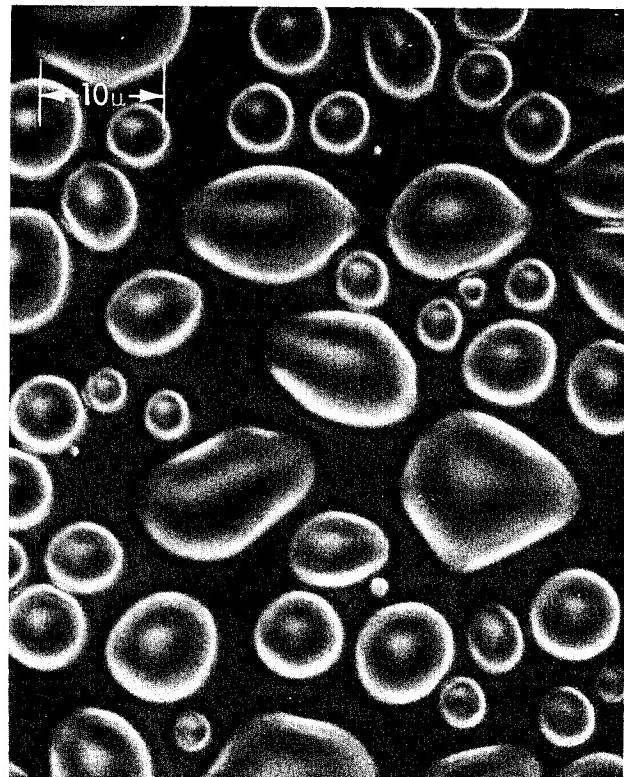


Figure 13—Droplets that formed on collector when polyvinyl chloride sample was heated to 70° C for 3 hours at 15 μ pressure.

The droplets shown in Figure 12 were photographed during test 7, near the start of the work on polyvinyl chloride. Repeated heating and cooling of the sample at various time periods, temperature variations, and pressure levels appeared to have little effect on the ability of the material to release its contaminating effluent.

The droplets shown in Figure 13 were formed during test 8. The photomicrographs of Figures 12 and 13 were taken at the lowest temperature at which any structure appeared.

Polyurethane

A sample of polyurethane was heated at 180°C for 3 hours at a pressure of 10^{-5} torr. The results are shown in Figure 14.

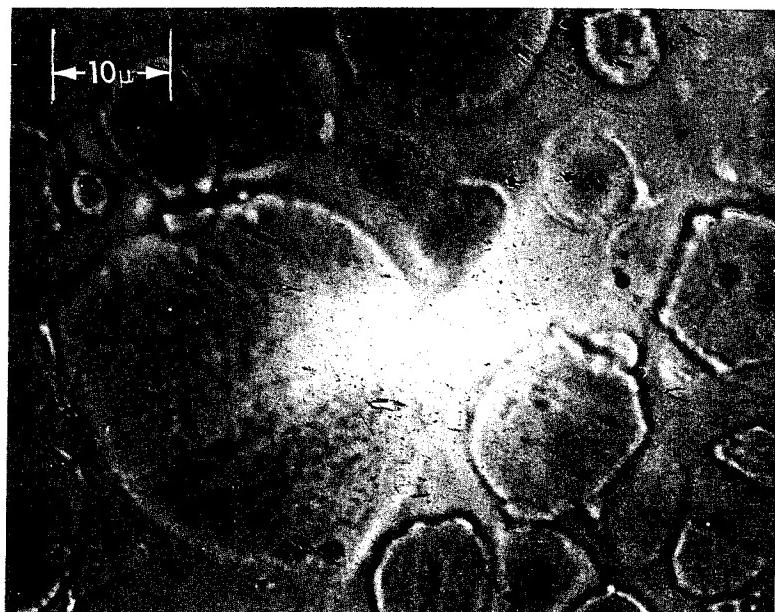


Figure 14—Effluent from polyurethane after sample was heated to 180°C for 3 hours at 10^{-5} torr.

Epoxy and RTV

Epoxy and RTV, two major classes of polymer commonly used in the aerospace industry, were studied, although the results are not represented by photomicrographs. The epoxy used was Armstrong A31, and regardless of the treatment, no condensable effluent was found on the slide surfaces. The material was heated to 300°C in vacuum of 10^{-7} torr for 160 hours without acquiring an effluent. Weight loss data taken for six variations of temperature or pressure averaged about 0.2% for a 5.0-g sample. The only noticeable sample change appeared to be a slight browning.

RTV-102 was used as an example of the class of silicone rubbers. Unlike the epoxy, this material readily gave up an effluent, which formed films. At 100°C and vacuum of 15 μ , heavy deposits of film formed, but without characteristics that were visible under the ordinary light microscope. Previous analytical experience with films formed from RTV's always seemed to be siloxanes, and the film from RTV-102 also had a greasy quality usually associated with the siloxanes. However, no attempts were made to justify the observation analytically.

DISCUSSION

Without some knowledge of the chemical nature of the effluent, it becomes impossible to ascribe a mechanism to the observed phenomena. A vapor is said to be congruent when the molecular species in the vapor is the same as that in the solid or liquid from which it comes. The dependence on temperature shown by this study would imply that chemical bonds are being broken and that the effluent is noncongruent. The case of polyurethane may be an exception, however, since 180°C is very close to the liquidus line and the contaminant may very well be recrystallized polyurethane.

The largest single factor that allowed these structures to remain on the slide was, of course, the temperature difference between the heated cell and the slide surface. Some minimum temperature is necessary in order to drive a solid into the vapor phase, and only a surface of lower temperature will allow the vapor to condense.

This was illustrated in the experiments with polyvinyl chloride. For this polymer, 70°C is near the required temperature of vaporization. The temperature variations were taken in 10°C increments without further attempt at refinement. At 60°C, the slides were examined for effluent after 5 minutes and after 16 hours at 15 μ ; they were examined again after 3 hours at 10⁻⁵ torr. No visible effluent resulted from any of these manipulations. The temperature of the same sample was then elevated to 70°C for 3 hours at 15 μ (see Figure 13).

Many experiments were performed using either time or pressure as the variable without noticeably affecting the results; only temperature seemed to be the determining variable. Thermocouples attached to both slide and cell gave the temperature calibration shown in Figure 15. These temperatures are not extremely different, as is so often the case where a liquid nitrogen cold finger is used to condense the effluent.

Temperature and pressure effects on the quartz crystal microbalance, which normally would be subtracted from final results to minimize error, here assumed magnitudes greater than the quantities being measured. An average of 18 exposures to the test conditions indicated a frequency shift of 2 cycles equal to

$$\frac{1}{3 \times 10^1} \times \frac{1}{1.4 \times 10^2} \times 10^{-8} = 2 \times 10^{-12} \text{ g}$$

in the area seen in Figure 6, while that of Figure 13 indicates a weight of about 10⁻¹⁰ g.

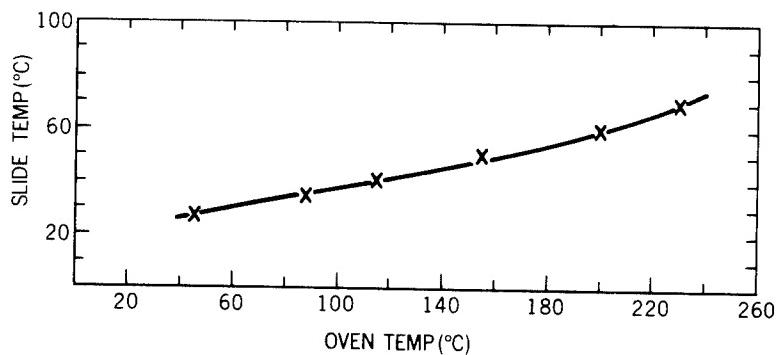


Figure 15—Temperature calibration showing slide temperature versus oven temperature.

CONCLUSIONS

In conclusion, an attempt has been made to illustrate that there are differences in the physical appearance of outgassed material of different polymers. From these experiments, it appears that sometimes it is easily possible to differentiate one class of polymer from another and that, by using very simple microscopic techniques, the extent of contamination can be realistically estimated.

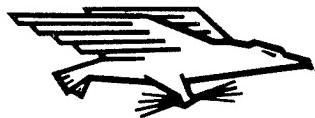
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